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# Matrix isolation and computational study of isodifluorodibromomethane ( $\text{F}_2\text{CBr}-\text{Br}$ ): A route to $\text{Br}_2$ formation in $\text{CF}_2\text{Br}_2$ photolysis

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The photolysis products of dibromodifluoromethane ( $\text{CF}_2\text{Br}_2$ ) were characterized by matrix isolation infrared and UV/Visible spectroscopy, supported by *ab initio* calculations. Photolysis at wavelengths of 240 and 266 nm of  $\text{CF}_2\text{Br}_2:\text{Ar}$  samples ( $\sim 1:5000$ ) held at  $\sim 5$  K yielded iso- $\text{CF}_2\text{Br}_2$  ( $\text{F}_2\text{CBrBr}$ ), a weakly bound isomer of  $\text{CF}_2\text{Br}_2$ , which is characterized here for the first time. The observed infrared and UV/Visible absorptions of iso- $\text{CF}_2\text{Br}_2$  are in excellent agreement with computational predictions at the B3LYP/aug-cc-pVTZ level. Single point energy calculations at the CCSD(T)/aug-cc-pVDZ level on the B3LYP optimized geometries suggest that the isoform is a minimum on the  $\text{CF}_2\text{Br}_2$  potential energy surface, lying some 55 kcal/mol above the  $\text{CF}_2\text{Br}_2$  ground state. The energies of various stationary points on the  $\text{CF}_2\text{Br}_2$  potential energy surface were characterized computationally; taken with our experimental results, these show that iso- $\text{CF}_2\text{Br}_2$  is an intermediate in the  $\text{Br}+\text{CF}_2\text{Br}\rightarrow\text{CF}_2+\text{Br}_2$  reaction. The photochemistry of the isoform was also investigated; excitation into the intense 359 nm absorption band resulted in isomerization to  $\text{CF}_2\text{Br}_2$ . Our results are discussed in view of the rich literature on the gas-phase photochemistry of  $\text{CF}_2\text{Br}_2$ , particularly with respect to the existence of a roaming atom pathway leading to molecular products. © 2010 American Institute of Physics. [doi:10.1063/1.3319567]

## I. INTRODUCTION

Due to their long-standing use as flame retardants, and potential for ozone depletion, the photochemistry of bromine-containing halocarbons (halons) has received extensive scrutiny.<sup>1–23</sup> Recent work has focused on elucidating the wavelength dependent mechanisms of the photochemical reactions that occur following ultraviolet (UV) excitation. Difluorodibromomethane ( $\text{CF}_2\text{Br}_2$ ; Halon 1202) is a prototypical halon, exhibiting a rich photochemistry that is not fully understood. The most basic question concerns the branching between two nearly isoenergetic dissociation channels: (1) a radical channel yielding  $\text{CF}_2\text{Br}+\text{Br}$  and (2) a molecular elimination channel yielding  $\text{CF}_2+\text{Br}_2$ .

The room temperature UV absorption spectrum of  $\text{CF}_2\text{Br}_2$  exhibits two broad features centered at  $\sim 188$  and  $\sim 226$  nm. The earliest flash photolysis study of  $\text{CF}_2\text{Br}_2$  by Mann and Thrush<sup>24</sup> in 1960 reported formation of  $\text{CF}_2$ , thus beginning a long and controversial saga concerning the UV photolysis products. In 1972, a gas-phase photolysis study at 260 nm revealed a product distribution that was consistent with the formation of  $\text{CF}_2\text{Br}$  radicals and Br atoms.<sup>25</sup> Later, prompt fluorescence from  $\text{CF}_2$  was observed in the 248 nm photolysis of  $\text{CF}_2\text{Br}_2$ ,<sup>26,27</sup> and emission from  $\text{Br}_2$  and Br was also observed,<sup>26</sup> findings which were taken to suggest that both channels were open at this wavelength. In 1984, the Lee group reported an inaugural molecular beam study of  $\text{CF}_2\text{Br}_2$  photodissociation at 248 nm using photofragment transla-

tional energy spectroscopy.<sup>22</sup> The only primary channel observed was C–Br bond fission; however, it was also found that  $\text{CF}_2$  was formed under collision free conditions, which was attributed to secondary photolysis of the  $\text{CF}_2\text{Br}$  radical. This required that the  $\text{CF}_2\text{Br}$  absorption cross section at 248 nm be sufficiently large so that the secondary photolysis step was fully saturated, giving the observed linear dependence of the  $\text{CF}_2$  signal on laser fluence. However, this assumption was later questioned in an ultrafast absorption study of the dissociation,<sup>21</sup> where the  $\text{CF}_2\text{Br}$  transient absorption spectrum was measured, and it was proposed that the observed  $\text{CF}_2$  photoproduct at 248 nm was formed via sequential cleavage of the two C–Br bonds.

More recent studies have examined the wavelength dependence of the photolysis. In 1983 Molina *et al.*<sup>28</sup> examined the photolysis in 1 atm of air at wavelengths of 206, 248, and 302 nm. Unity quantum yields were determined for the two primary products,  $\text{CF}_2\text{O}$  and  $\text{Br}_2$ , which were taken to indicate that the primary photolysis step was C–Br bond fission. Ravishankara and co-workers<sup>29</sup> measured the quantum yield of Br atom formation following photolysis of  $\text{CF}_2\text{Br}_2$  at 298 nm and wavelengths of 193, 222, and 248 nm. The Br atom quantum yield increased from  $1.01 \pm 0.15$  at 248 nm to  $1.96 \pm 0.27$  at 193 nm. A later study by the same group found that the  $\text{CF}_2$  quantum yield at 248 nm was  $1.15 \pm 0.30$ .<sup>13</sup> In 2000, Kable and co-workers<sup>11</sup> reported a detailed study of the energy disposal in the  $\text{CF}_2$  photofragment from  $\text{CF}_2\text{Br}_2$  photolysis at wavelengths in the range 260–223 nm. Analysis of the  $\text{CF}_2$  energy disposal in combination with available

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thermochemical data showed that at all wavelengths the counterfragment was not  $\text{Br}_2$ , but rather two bromine atoms. The energetic onset of  $\text{CF}_2$  production was determined to be  $460 \pm 3$  kJ/mol, corresponding to a wavelength of  $260 \pm 1.5$  nm, and it was proposed that this threshold corresponded to the top of a barrier in the exit channel.

These studies paint a consistent picture of the UV photodissociation of  $\text{CF}_2\text{Br}_2$  as involving C–Br fission in an initial step, followed by a second C–Br fission as a result of intramolecular vibrational energy redistribution, which leads to  $\text{CF}_2$  production for wavelengths below 260 nm. However, recent studies have also indicated the existence of a  $\text{Br}_2$  elimination channel in small yield under collision free conditions. This was first shown for photolysis at 193 nm in a molecular beam by Huber and co-workers.<sup>17</sup> Later, in ion imaging experiments, Park *et al.*<sup>8</sup> reported a “trace” amount of  $\text{Br}_2$  photoproduct following excitation at 234 nm. More recently, Lin and co-workers<sup>5</sup> probed  $\text{Br}_2$  directly using cavity ring down spectroscopy, and reported a quantum yield of 0.04 for the molecular channel at 248 nm. We note that the  $\text{Br}_2$  channel has also been observed, up to a reported quantum yield of  $\sim 0.25$ , in infrared (IR) multiphoton dissociation experiments.<sup>15,23</sup>

In this work, we have examined the photolysis of  $\text{CF}_2\text{Br}_2$  in an Ar matrix at  $\sim 5$  K at wavelengths of 240 and 266 nm, above and below, respectively, the threshold for  $\text{CF}_2$  production reported by Kable and co-workers.<sup>11</sup> The primary goal of this study was to observe the isoform of this molecule ( $\text{F}_2\text{CBr}-\text{Br}$ ), building upon our recent observation and characterization of iso- $\text{CF}_2\text{I}_2$ .<sup>30</sup> There are very few previous condensed phase studies of  $\text{CF}_2\text{Br}_2$  photolysis.<sup>7,31,32</sup> In 1969, photolysis of  $\text{CF}_2\text{Br}_2$  in a neat solution frozen at 77 K was reported, and the formation of  $\text{Br}_2$  inferred by chemical trapping.<sup>31</sup> In 1978, Jacox<sup>32</sup> reported the photolysis of  $\text{CF}_2\text{Br}_2$  isolated in solid Ar ( $\text{CF}_2\text{Br}_2:\text{Ar}=1:270$ ), in a study that was focused on characterization of the  $\text{CF}_2\text{Br}$  radical. In that work strong absorptions due to the dimerization products  $\text{C}_2\text{F}_4$  and  $\text{C}_2\text{F}_4\text{Br}_2$  were observed, in addition to the target radical. The studies reported here were carried out in much more dilute matrices ( $\text{CF}_2\text{Br}_2:\text{Ar} \sim 1:5000$ ), in an attempt to avoid parent aggregation.

This work complements earlier studies of the isoforms of  $\text{CH}_2\text{X}_2$  ( $\text{X}=\text{Cl}, \text{Br}, \text{I}$ ), which were isolated and characterized under matrix isolation conditions by Maier and co-workers.<sup>33,34</sup> Many experimental and theoretical studies of these species have since been carried out, which illustrate novel chemistry for the isopolyhalomethanes.<sup>35–46</sup> For example, iso- $\text{CH}_2\text{I}_2$  is the primary species responsible for the cyclopropanation of olefins when  $\text{CH}_2\text{I}_2$  is photolyzed in the presence of olefins.<sup>37</sup> In Maier’s work, a number of possible resonance structures for the iso- $\text{CH}_2\text{XY}$  halons were considered.<sup>34</sup> The experimental data were most consistent with an ion-pairlike structure:  $\text{CH}_2\text{X}^+-\text{Y}^-$ , where the positive charge resided on C or X, the latter giving a  $\text{C}=\text{X}$  double bond.<sup>47,48</sup> Due to the pronounced stability and singlet ground state of  $\text{CF}_2$ , study of the analogous iso- $\text{CF}_2\text{X}_2$  species should be illuminating as to the effect of substitution on the relative contribution of the various possible resonance structures.

An outline of the paper is as follows. Section II presents details of the experimental and computational methodology. Section III presents our key results, which are discussed in the light of previous experimental and theoretical studies. Finally, Sec. IV provides a summary and key conclusions of this work.

## II. EXPERIMENTAL AND THEORETICAL METHODS

The matrix isolation experiments utilized a cryostat based upon a closed cycle two-stage He dispex (ARS Displex DE-204S). On the cold tip was mounted an optical sample holder containing a 25.4 mm diameter  $\text{CaF}_2$  or  $\text{KBr}$  window. A loop of 1.0 mm diameter. Indium wire was placed between window and sample holder to ensure good thermal contact, while a thin layer of cryogenic grease (Apiezon N) was placed between the cold tip and sample mount for the same purpose. A nickel-plated copper radiation shield with two circular ports enclosed the cold tip. The dispex and attached radiation shield were inserted into a clamped vacuum shroud and sealed with a double O-ring seal that allowed the sample assembly to be rotated under vacuum. The vacuum shroud was equipped with four orthogonal window mounts. On two opposing mounts were attached 50.8 mm diameter polished  $\text{KBr}$  windows. A 10 mm thick custom-made flange that coupled to a commercial pulsed valve was attached to a third mount. The pumping station consisted of a liquid-nitrogen trapped diffusion pump (Varian H-4) backed by a scroll pump (Edwards XDS-10), connected to the cryostat via a NW-40 port welded onto the vacuum shroud. An ionization gauge mounted at this port monitored the vacuum in the cryostat. The temperature at the cold tip and sample window were monitored simultaneously using two Si diodes that were interfaced to a temperature controller (Lakeshore 330).

IR absorption spectra were obtained with an Fourier transform infrared spectrometer (Mattson, Galaxy series) equipped with a deuterated triglycine sulfate detector, which was purged at a flow rate of 20 L/min using a purge gas generator (Parker-Balston 75–52A). The IR spectra were recorded at typically  $1\text{ cm}^{-1}$  resolution and averaged over 128 scans. Ultraviolet/visible (UV/VIS) absorption spectra were obtained with an Agilent 8453 diode array spectrophotometer. The reference spectra for both IR and UV/VIS were recorded for the cold sample holder immediately prior to matrix deposition, and the entire cryostat was mounted on a home-built rail system that allowed quick interchange between spectrometers.

The  $\text{CF}_2\text{Br}_2$  sample (Synquest Laboratories, 99% stated purity, used without further purification) was premixed in a 0.5 L stainless steel mixing tank with high purity argon, resulting in a mixture that was  $\sim 1:5000$   $\text{CF}_2\text{Br}_2:\text{Ar}$ . Before each experiment the sample line was pumped under vacuum in order to remove any volatile impurities. The mixture was deposited onto the cold window held at  $\sim 5$  K using the pulsed deposition method with a solenoid activated pulsed valve (Parker-Hannifan, General Valve Division, Iota-1); typical conditions were 1 ms pulse duration, 10 Hz repetition rate, 1 h deposition time, and 3 bar backing pressure.

Following deposition, the cold window was irradiated with laser light at 266 nm, generated from the fourth harmonic of a pulsed neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Continuum Minilite), or 240 nm, generated from the frequency doubled output of a dye laser system (Lambda-Physik Scanmate 2E) operating on Coumarin 480 dye, pumped by the third harmonic (355 nm) of a Nd:YAG laser (Continuum NY-61). The photolysis beam was expanded using a 4:1 beam expander to fill the cold window and avoid damage to the KBr windows. Typical irradiation times were 1.5 h at 240 nm (10 ns pulses, 1 mJ/pulse, and 10 Hz), and 5 h at 266 nm (5 ns pulses, 2.3 mJ/pulse, and 5 Hz). Note that the gas-phase absorption cross section of the parent at 210 K is around 30 times larger at 240 nm than at 266 nm.<sup>49</sup> All spectra were transferred to a spreadsheet and analysis program (Origin 8.0) for subsequent workup.

Calculations were carried out on a personal computer using the GAUSSIAN 98 or GAUSSIAN 09 suite of electronic structure programs.<sup>50,51</sup> Geometry optimization was performed using the B3LYP and Möller-Plesset perturbation theory to second order (MP2) methods with a series of cc-pVXZ (Ref. 52) and aug-cc-pVXZ (X=D, T, and Q) basis sets, which constitute a logical sequence that converges toward the basis set limit. These basis sets have been shown to recover some of the correlation energy of the valence electrons,<sup>52</sup> an important feature in describing relatively weak bonding situations. In the aug-cc-pVXZ series, it has been found that, within a very tight error bar, the geometrical parameters are almost converged at the aug-cc-pVDZ step with respect to a further increase in the basis set description. Thus, for relaxed ground state potential energy surface scans along relevant geometrical parameters, the aug-cc-pVDZ basis set was considered sufficient to provide upper limits for relative energies between stationary points. To obtain a more quantitative description of the relative energies between selected stationary points, single point energy calculations were performed at the CCSD(T)/aug-cc-pVDZ level of theory using the optimized B3LYP/aug-cc-pVTZ structures.

### III. RESULTS AND DISCUSSION

#### A. Matrix IR spectroscopy and computational studies of iso-CF<sub>2</sub>Br<sub>2</sub>

Figure 1 shows matrix IR spectra of (a) an as-deposited CF<sub>2</sub>Br<sub>2</sub>:Ar (1:5000) sample, (b) a difference spectrum following 240 nm irradiation of a freshly deposited sample, (c) a difference spectrum following 240 nm irradiation of a freshly deposited sample and subsequent annealing to 35 K, and (d) the predicted IR spectra of iso-CF<sub>2</sub>Br<sub>2</sub> at the B3LYP/aug-cc-pVTZ level. Prior to irradiation [Fig. 1(a)], prominent absorptions at 820, 1080, and 1142 cm<sup>-1</sup> are observed, consistent with the known Ar matrix spectrum of CF<sub>2</sub>Br<sub>2</sub>, measured by Jacox.<sup>32</sup> Following photolysis at 240 nm [Fig. 1(b)], strong absorptions due to CF<sub>2</sub> are observed, and new bands appear at 1188 and 1240 cm<sup>-1</sup>, which we assign to the symmetric ( $\nu_1$ ) and antisymmetric ( $\nu_7$ ) C–F stretching modes of iso-CF<sub>2</sub>Br<sub>2</sub>. The origin of these bands was confirmed in annealing experiments, in which the temperature of the cold

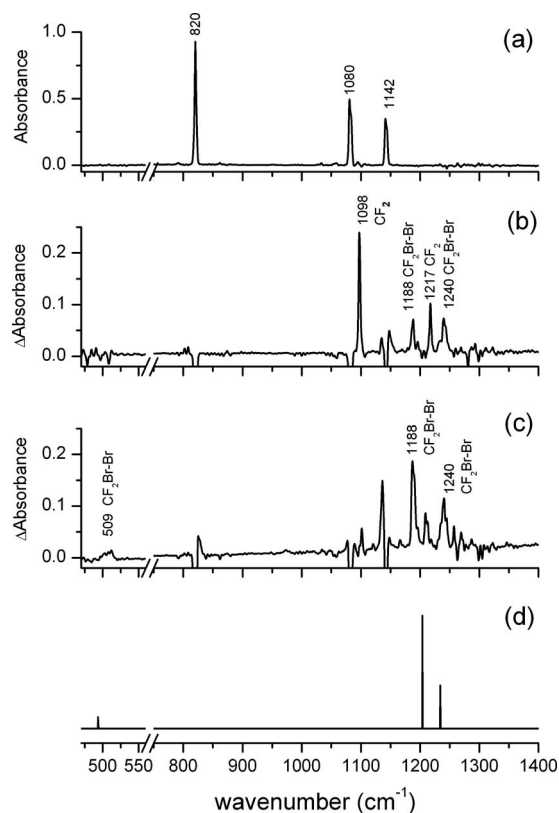


FIG. 1. (a) IR spectrum of a CF<sub>2</sub>Br<sub>2</sub>:Ar matrix (~1:5000) at ~5 K. (b) Difference spectrum obtained following irradiation of an as-deposited matrix at 240 nm (details in the text). (c) Difference spectrum obtained following annealing of a CF<sub>2</sub>Br<sub>2</sub>:Ar matrix that was first irradiated at 240 nm. (d) B3LYP/aug-cc-pVTZ predicted IR spectrum of iso-CF<sub>2</sub>Br<sub>2</sub>.

window was raised to 35 K and subsequently recooled to ~5 K. Postannealed spectra show loss of CF<sub>2</sub> and an increase in the 1188, 1240 cm<sup>-1</sup> absorptions; in addition, a new band at 509 cm<sup>-1</sup> is also apparent [Fig. 1(c)], which is assigned to the C–Br stretching mode ( $\nu_3$ ) of iso-CF<sub>2</sub>Br<sub>2</sub>. The positions and relative intensities of these absorptions are in excellent agreement with predictions for iso-CF<sub>2</sub>Br<sub>2</sub> at the B3LYP/aug-cc-pVTZ level [Fig. 1(d) and Table I]. The increase in intensity of the iso-CF<sub>2</sub>Br<sub>2</sub> absorptions with annealing is consistent with previous experiments on the related CF<sub>2</sub>I<sub>2</sub> system.<sup>30</sup> Note also that the strong feature observed near the parent absorption at 1142 cm<sup>-1</sup> in Fig. 1(c) reflects changes in the spectrum of the unphotolyzed parent upon

TABLE I. Vibrational frequencies of iso-CF<sub>2</sub>Br<sub>2</sub> determined at the B3LYP/aug-cc-pVTZ level of theory.

Vibrational mode	Symmetry	Vibrational frequency (cm <sup>-1</sup> )	Intensity (km/mol)
$\nu_1$	A'	1203	769
$\nu_2$	A'	660	5
$\nu_3$	A'	493	79
$\nu_4$	A'	212	1.7
$\nu_5$	A'	143	78
$\nu_6$	A'	56	1
$\nu_7$	A''	1234	295
$\nu_8$	A''	268	0.3
$\nu_9$	A''	56	1



TABLE II. Fully optimized geometrical parameters for the iso-CF<sub>2</sub>Br<sub>2</sub> species. Angles are given in degrees and bond lengths in angstroms.

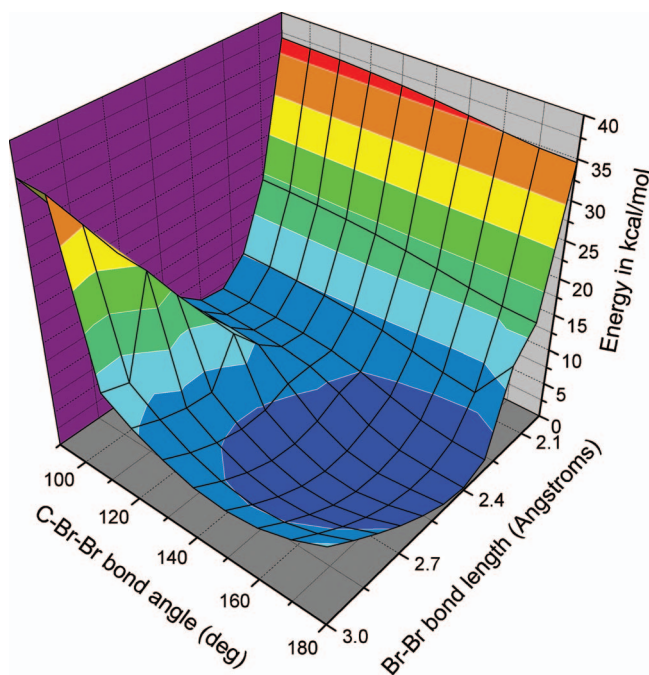
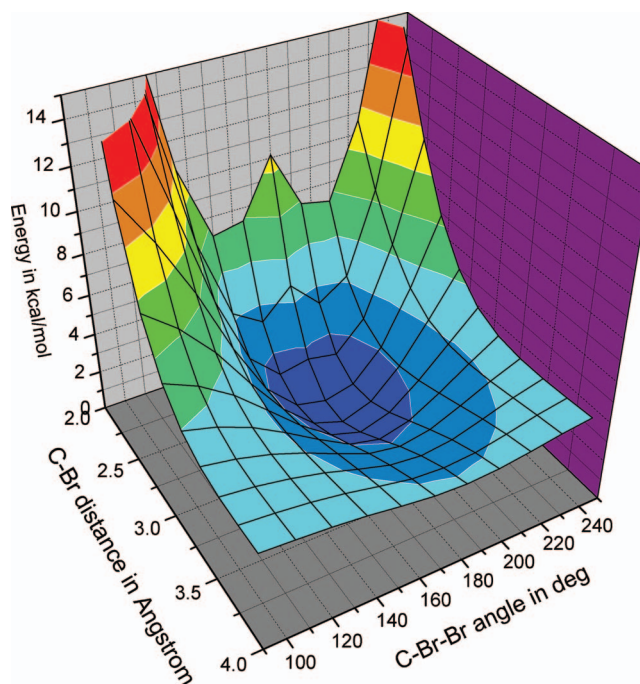
Method	C–F	C–Br	Br–Br	F–C–F	F–C–Br	C–Br–Br
B3LYP/cc-pVDZ	1.299	2.084	2.526	108.4	119.7	160.1
B3LYP/cc-pVTZ	1.294	2.050	2.520	108.6	119.6	158.8
B3LYP/cc-pVQZ	1.294	2.022	2.529	108.8	119.7	157.6
B3LYP/aug-cc-pVDZ	1.306	1.987	2.567	108.7	120.0	156.5
B3LYP/aug-cc-pVTZ	1.296	2.026	2.528	108.6	119.6	157.4
B3LYP/aug-cc-pVQZ	1.295	2.016	2.530	108.8	119.6	157.1
MP2/cc-pVDZ	1.314	1.848	2.622	109.7	119.4	143.7
MP2/cc-pVTZ	1.307	1.824	2.565	109.6	119.8	141.9
MP2/cc-pVQZ	1.305	1.813	2.554	109.7	120.0	140.9
MP2/aug-cc-pVDZ	1.329	1.821	2.633	109.3	119.7	139.1
MP2/aug-cc-pVTZ	1.310	1.814	2.570	109.6	119.8	139.6
MP2/aug-cc-pVQZ	1.306	1.806	2.557	109.7	120.1	139.5

annealing, which was confirmed by annealing a freshly deposited CF<sub>2</sub>Br<sub>2</sub> sample (Figure S1, supporting information).<sup>53</sup>

Further support for our experimental observation of the iso-form of CF<sub>2</sub>Br<sub>2</sub> comes from theory, which shows that iso-CF<sub>2</sub>Br<sub>2</sub> is a minimum on the CF<sub>2</sub>Br<sub>2</sub> potential energy surface (PES). As noted above, the predicted B3LYP/aug-cc-pVTZ IR spectrum is in good agreement with our experimental results (Fig. 1). The calculated vibrational frequencies for the isoform at this level of theory are given in Table I, while Table II lists the fully optimized structural parameters determined at the B3LYP and MP2 levels of theory, with different basis sets. We also calculated the relaxed PES along the Br–Br stretching and C–Br–Br bending coordinates at the B3LYP/cc-pVDZ level of theory, which is shown in Fig. 2. The isoform is clearly a minimum at this level of theory; note, however, the shallow ridge along a Br–Br dis-

tance of  $\sim 2.3$  Å, near the equilibrium bond length of Br<sub>2</sub>. The optimized structure along this ridge clearly resembles a CF<sub>2</sub>–Br<sub>2</sub> complex. This complex was characterized by performing a second relaxed PES calculation along the C–Br stretching and C–Br–Br bending coordinates, with the Br–Br distance fixed at the equilibrium value of Br<sub>2</sub>; this PES is shown in Fig. 3. In contrast to iso-CF<sub>2</sub>Br<sub>2</sub>, where the calculated equilibrium C–Br–Br bond angle is 157° at the B3LYP/aug-cc-pVTZ level, the calculated minimum for the complex corresponds to linear C–Br–Br, i.e., a bond angle of 180°. At this level of theory, there is no barrier to dissociation of iso-CF<sub>2</sub>Br<sub>2</sub> into CF<sub>2</sub>+Br<sub>2</sub>, a point to which we shall return.

Density functional theory (DFT) calculations using the B3LYP functional are often of limited value for characterizing weakly bound systems where dispersion contributions

FIG. 2. Relaxed potential energy surface of iso-CF<sub>2</sub>Br<sub>2</sub> calculated at the B3LYP/cc-pVDZ level of theory.FIG. 3. Relaxed potential energy surface for the CF<sub>2</sub>–Br<sub>2</sub> complex calculated at the B3LYP/cc-pVDZ level of theory. The Br–Br distance was fixed at the equilibrium separation of Br<sub>2</sub>.

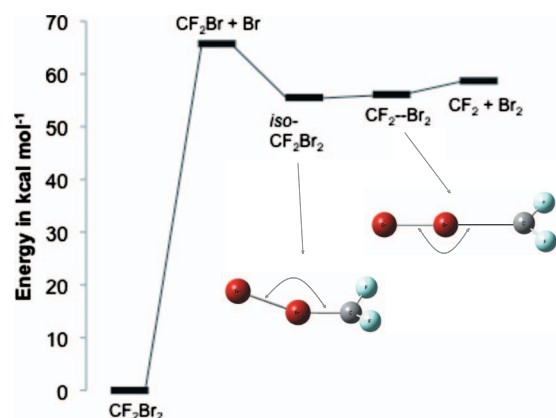


FIG. 4. Calculated stationary points on the CF<sub>2</sub>Br<sub>2</sub> potential energy surface. The energies were calculated at the CCSD(T)/aug-cc-pVDZ level on structures optimized at the B3LYP/aug-cc-pVTZ level.

are significant, and therefore higher level [CCSD(T)/aug-cc-pVDZ] calculations were performed on selected stationary points on the CF<sub>2</sub>Br<sub>2</sub> PES, using structures optimized at the B3LYP/aug-cc-pVTZ level. The results of these calculations are shown in Fig. 4. The calculated Br–CF<sub>2</sub>Br bond energy at this level of theory is in quantitative agreement with the best experimental value.<sup>11</sup> At this level of theory, the energy of iso-CF<sub>2</sub>Br<sub>2</sub> is similar to that of the CF<sub>2</sub>–Br<sub>2</sub> complex, both of which lie below the energetic thresholds to C–Br bond cleavage or Br<sub>2</sub> elimination. Our computational results are in very close agreement with the previous calculations of Cameron and Bacskay,<sup>10</sup> with one notable exception. In that work, they searched for and found a transition state (TS) for the Br+CF<sub>2</sub>Br→CF<sub>2</sub>+Br<sub>2</sub> reaction; the structure of this TS bears similarities to that determined here for iso-CF<sub>2</sub>Br<sub>2</sub>. However, because optimization was performed to characterize a saddle point rather than a minimum energy structure, no report was given of a minimum corresponding to the iso-form. Our results show that iso-CF<sub>2</sub>Br<sub>2</sub> is a minimum on the CF<sub>2</sub>Br<sub>2</sub> PES and an intermediate in the Br+CF<sub>2</sub>Br→CF<sub>2</sub>+Br<sub>2</sub> reaction. Note that Cameron and Bacskay searched for but did not find a TS on the ground state surface, which linked the parent CF<sub>2</sub>Br<sub>2</sub> to molecular products (CF<sub>2</sub>+Br<sub>2</sub>). Clearly, more theoretical studies are warranted to map out this region of the PES, which is of potential importance in understanding the branching between the radical and molecular decomposition channels in the gas phase.

When the calculated geometrical parameters using the MP2 wave function and the B3LYP density functional are compared (Table II), the parameter most sensitive to the description is the C–Br–Br angle (C–Br–Br= ~157°/140° at the B3LYP/MP2 levels, respectively). In fact, the calculated value of the C–I–I angle in the H<sub>2</sub>C–I–I isomer of CH<sub>2</sub>I<sub>2</sub> at the MP2 level of theory is also underestimated when compared to a rather good B3LYP description that agrees well with the computed CASPT2 geometry of this isomer.<sup>54</sup> Moreover, the constrained parameters corresponding to the optimized MP2 geometrical parameters lie close to the optimized B3LYP minimum (Fig. 3), particularly given the shallowness in this region, which indicates that multiple confor-

mations are accessible, the calculated zero point energy of the fully optimized MP2 minimum being 6.7 kcal/mol.

As noted in Sec. I, there has been significant previous work on the related iso-CH<sub>2</sub>X<sub>2</sub> species, where the experimental data are most consistent with an ion-pairlike structure: CH<sub>2</sub>X<sup>+</sup>–Y<sup>–</sup>.<sup>34</sup> For example, the C–I stretching frequency of iso-CH<sub>2</sub>I<sub>2</sub> is 712 cm<sup>–1</sup> (Ar matrix),<sup>34</sup> similar to that determined by us for CH<sub>2</sub>I<sup>+</sup> in the gas phase (755 cm<sup>–1</sup>).<sup>47,48</sup> In the iso-CF<sub>2</sub>Br<sub>2</sub> system, the calculated Br–Br bond length (Table I) is significantly larger than in free Br<sub>2</sub>, and the calculated (Mulliken) atomic charge on the terminal Br atom for iso-CF<sub>2</sub>Br<sub>2</sub> at the B3LYP/aug-cc-pVTZ level is negative and similar in magnitude to that determined for iso-CH<sub>2</sub>Br<sub>2</sub> at the same level of theory.

## B. Comparison of matrix IR results with previous work

We now compare our results with the previous study of Jacox.<sup>32</sup> In that work, the photolysis of more concentrated samples (CF<sub>2</sub>Br<sub>2</sub>:Ar=1:270) yielded prominent absorptions assigned to C<sub>2</sub>F<sub>4</sub>, C<sub>2</sub>F<sub>4</sub>Br<sub>2</sub>, and the target CF<sub>2</sub>Br radical. In our work, bands of the CF<sub>2</sub>Br radical at 1136 and 1198 cm<sup>–1</sup> were indeed observed in samples photolyzed at 266 nm (Fig. S2, supporting information),<sup>53</sup> in addition to those of CF<sub>2</sub> and iso-CF<sub>2</sub>Br<sub>2</sub>. The absence of these bands following 240 nm photolysis (Fig. 1) is consistent with the energetic threshold for CF<sub>2</sub> formation observed by Kable and co-workers.<sup>11</sup> While there is no evidence of C<sub>2</sub>F<sub>4</sub> in our spectra (Fig. 1), prior studies of the matrix photolysis of CF<sub>2</sub>I<sub>2</sub>:Ar samples revealed prominent C<sub>2</sub>F<sub>4</sub> absorptions under conditions where aggregation was indicated. We therefore believe that the dimerization products (C<sub>2</sub>F<sub>4</sub>, C<sub>2</sub>F<sub>4</sub>Br<sub>2</sub>) observed by Jacox reflect parent aggregation in the more concentrated matrix. Jacox did report the absorptions at 1188 and 1240 cm<sup>–1</sup> that we assign to iso-CF<sub>2</sub>Br<sub>2</sub>; the former was unassigned, while the latter was assigned to C<sub>2</sub>F<sub>4</sub>Br<sub>2</sub>. To assess the degree (if any) to which C<sub>2</sub>F<sub>4</sub>Br<sub>2</sub> contributed to our spectra, we obtained a sample of the pure compound (Synquest Laboratories) and measured the matrix IR spectrum in Ar at a mixing ratio of ~1:1000. The observed and predicted (B3LYP/aug-cc-pVTZ) IR spectra, provided in Figure S3 in the supporting information,<sup>53</sup> demonstrate conclusively that C<sub>2</sub>F<sub>4</sub>Br<sub>2</sub> is not present in any of the spectra we obtained following photolysis of CF<sub>2</sub>Br<sub>2</sub> in Ar matrices.

In her 1978 study,<sup>32</sup> Jacox also observed a shoulder at 1235 cm<sup>–1</sup> which was not assigned. This band appeared in several of our spectra as a shoulder on the 1240 cm<sup>–1</sup> absorption, which may suggest that it corresponds to a site splitting in the matrix, or to the presence of another conformer that is locally stabilized.

## C. Electronic spectroscopy and photochemistry of iso-CF<sub>2</sub>Br<sub>2</sub>

Thus far, we have focused on the vibrational spectroscopy of the isospecies. Maier and co-workers<sup>33,34,55</sup> measured the electronic spectra of matrix isolated iso-CH<sub>2</sub>I<sub>2</sub>, and reported two bands, a weak band in the visible centered at 545 nm and a stronger band centered at 370 nm. For

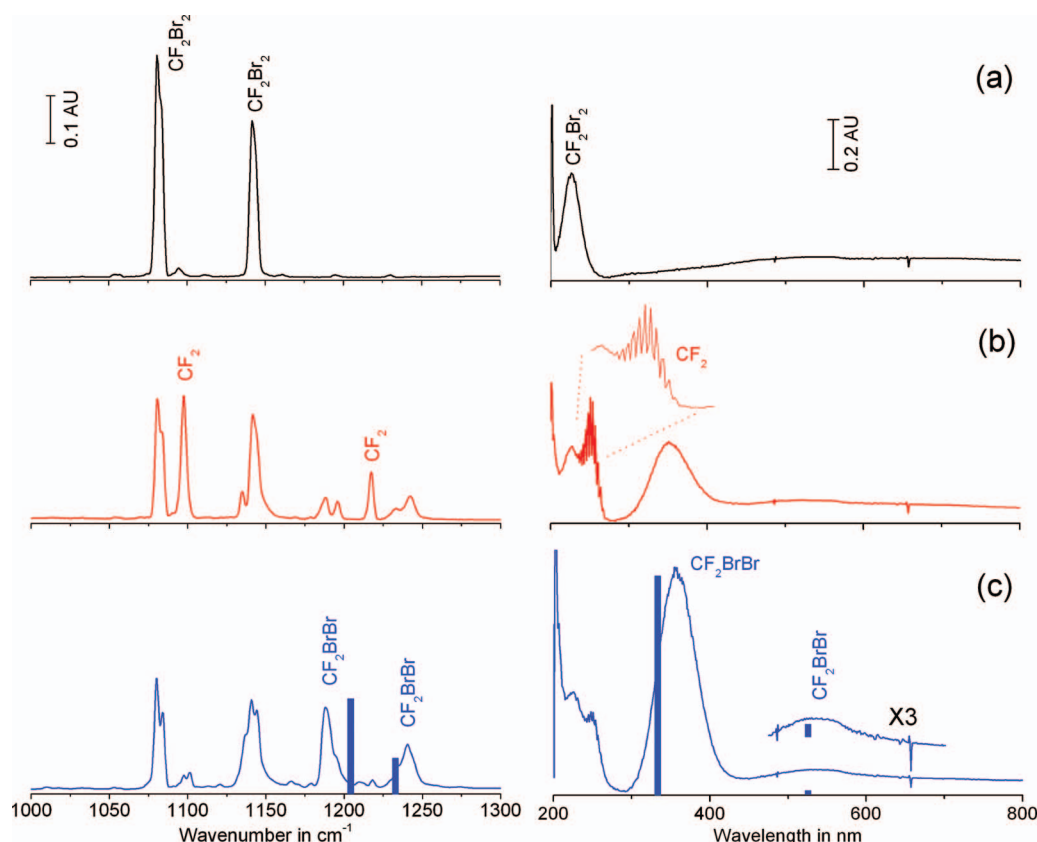


FIG. 5. (a) IR and UV/Visible spectra of a  $\text{CF}_2\text{Br}_2$ :Ar matrix at  $\sim 5$  K. (b) Spectra following irradiation at 240 nm. (c) Spectra following annealing to 35 K and recooling to 5 K. The bars in these spectra are predictions at the (TD)B3LYP/aug-cc-pVTZ level.

iso- $\text{CH}_2\text{Br}_2$ , only a band at  $\sim 360$  nm was observed.<sup>34</sup> We performed time-dependent density functional theory (TD-DFT) calculations (TDB3LYP/aug-cc-pVTZ) on the optimized iso- $\text{CF}_2\text{Br}_2$  structure to predict vertical excitation energies and oscillator strengths of the prominent electronic transitions. These calculations predict a weak ( $f=0.005$ ) band in the visible ( $\lambda_{\text{max}}=528$  nm), assigned to the  $1^1\text{A}' \rightarrow 2^1\text{A}'$  transition, and a strong ( $f=0.27$ ) band in the near-UV ( $\lambda_{\text{max}}=331$  nm), assigned to the  $1^1\text{A}' \rightarrow 3^1\text{A}'$  transition. Figure 5 compares side-by-side the IR and UV/Visible spectra of (a) an as-deposited  $\text{CF}_2\text{Br}_2$ :Ar sample, (b) the sample after photolysis at 240 nm, and (c) the sample following annealing to 35 K. In addition to the strong  $\text{S}_0\text{--}\text{S}_1$  transition of  $\text{CF}_2$ , which is vibrationally resolved, two new bands ( $\lambda_{\text{max}}=359, 536$  nm) appear upon photolysis and dramatically increase upon annealing, correlating with the IR absorptions assigned to iso- $\text{CF}_2\text{Br}_2$ . The band positions and relative intensities (359 nm band  $\sim 20$  times more intense) are in good agreement with the TDDFT predictions.

To probe the photochemistry of the isospecies, we irradiated at 355 nm (10 Hz, 6 mJ/pulse, and 30 min) a sample obtained according to the protocol developed above. The IR (Fig. 6) and UV/Visible spectra show nearly complete destruction of the isomer bands and growth of bands belonging to the normal isomer of  $\text{CF}_2\text{Br}_2$ .

#### D. Comparison of matrix and gas-phase photochemistry of $\text{CF}_2\text{Br}_2$

We now compare the matrix photochemistry with that previously observed in the gas phase. In the gas phase, UV

excitation leads predominantly to C–Br bond cleavage and the formation of the  $\text{CF}_2\text{Br}$  radical.<sup>22</sup> At wavelengths below 260 nm, the nascent  $\text{CF}_2\text{Br}$  radical spontaneously dissociates, producing  $\text{CF}_2$  and a second Br atom.<sup>8,11,21</sup> Recent experiments have also indicated a small (0.04 quantum yield) contribution from a direct  $\text{Br}_2$  elimination channel.<sup>5</sup> Consistent with these observations, we find very weak  $\text{CF}_2\text{Br}$  absorptions following 240 nm photolysis of matrix isolated samples (Fig. 1); these are slightly stronger when photolyzing at 266 nm (Fig. S2). Based on the calculations and the experimental observations described above, we propose the following sequence of reactions in the matrix:

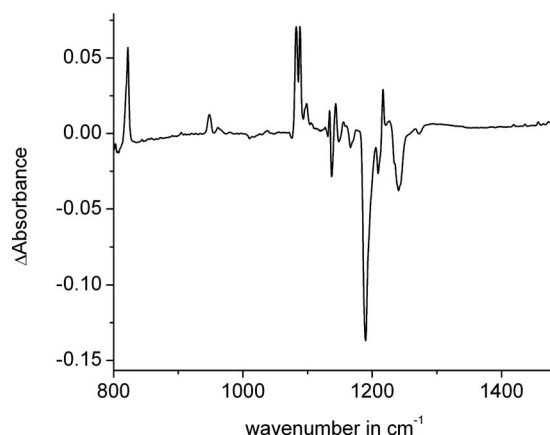
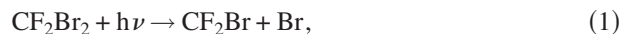


FIG. 6. Difference IR spectrum obtained following 355 nm irradiation of matrix isolated iso- $\text{CF}_2\text{Br}_2$ . The IR absorptions (1188, 1240  $\text{cm}^{-1}$ ) of the isoform decrease, while the parent  $\text{CF}_2\text{Br}_2$  bands increase.





Initial excitation Eq. (1) leads primarily to C–Br bond cleavage. In the matrix, the caged photofragments recombine, forming iso-CF<sub>2</sub>Br<sub>2</sub> Eq. (2), which can be trapped or react to produce molecular products [Eq. (3)]. The CF<sub>2</sub>Br radicals that do not immediately recombine can further dissociate to form CF<sub>2</sub> Eq. (4); note that CF<sub>2</sub>Br has a broad and unstructured UV absorption band peaking near 255 nm.<sup>21</sup> After annealing to 35 K, the CF<sub>2</sub>+Br<sub>2</sub> (or 2Br) and CF<sub>2</sub>Br+Br fragments recombine to form iso-CF<sub>2</sub>Br<sub>2</sub>.

The proposed mechanism for formation of molecular (CF<sub>2</sub>+Br<sub>2</sub>) products in the gas phase involved a roaming atom mechanism, although this term was not used, in that it was suggested that the departing Br fragment moved to form a Br–Br bond (i.e., forming iso-CF<sub>2</sub>Br<sub>2</sub>), followed by Br<sub>2</sub> elimination.<sup>5</sup> The roaming atom mechanism was first implicated in the photodissociation of formaldehyde,<sup>56–61</sup> and has since been evidenced in other photochemical reactions.<sup>62–66</sup> This work does not provide any evidence for the existence of roaming in CF<sub>2</sub>Br<sub>2</sub> photodissociation, yet the results presented here clearly show that iso-CF<sub>2</sub>Br<sub>2</sub> is an intermediate in the reaction: Br+CF<sub>2</sub>Br→CF<sub>2</sub>+Br<sub>2</sub>, and thereby confirm that in principle such a pathway is possible. Conclusive evidence of a roaming type mechanism in CF<sub>2</sub>Br<sub>2</sub> photolysis leading to molecular products will require additional experimental and theoretical studies.

#### IV. CONCLUSIONS

We report the first observation of iso-CF<sub>2</sub>Br<sub>2</sub>, a weakly bound isomer of CF<sub>2</sub>Br<sub>2</sub>. The isomer was observed in matrix IR and UV/Visible spectra obtained following photodissociation of CF<sub>2</sub>Br<sub>2</sub> at either 240 or 266 nm in an Ar matrix (CF<sub>2</sub>Br<sub>2</sub>:Ar=1:5000) at ~5 K. The assignments are supported by theory, which shows that iso-CF<sub>2</sub>Br<sub>2</sub> is a minimum on the CF<sub>2</sub>Br<sub>2</sub> PES, and by annealing experiments, which reveal that iso-CF<sub>2</sub>Br<sub>2</sub> is formed by the recombination of CF<sub>2</sub>Br with Br, and CF<sub>2</sub> with Br<sub>2</sub> or 2Br, in the matrix. In contrast to a previous report of CF<sub>2</sub>Br<sub>2</sub> photolysis in Ar matrices which utilized more concentrated samples (CF<sub>2</sub>Br<sub>2</sub>:Ar=1:270), we do not observe the dimerization products C<sub>2</sub>F<sub>4</sub> and C<sub>2</sub>F<sub>4</sub>Br<sub>2</sub>, a fact that we ascribe to reduced aggregation in our more dilute (CF<sub>2</sub>Br<sub>2</sub>:Ar~1:5000) matrices.

Our experiments indicate that iso-CF<sub>2</sub>Br<sub>2</sub> is an intermediate in the Br+CF<sub>2</sub>Br→CF<sub>2</sub>+Br<sub>2</sub> reaction, and therefore can be considered to play an important role in the formation of molecular products from CF<sub>2</sub>Br<sub>2</sub> photolysis in condensed phases. This isomer may also be important in the gas-phase photochemistry of CF<sub>2</sub>Br<sub>2</sub>, if roaming is indeed the primary mechanism leading to formation of molecular products. The

photochemistry of the isoform was investigated; excitation into the strong 359 nm absorption of this species results in isomerization to CF<sub>2</sub>Br<sub>2</sub>.

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